IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C., UNITED STATES of AMERICA


UNITED STATES UTILITY PATENT APPLICATION


for


Catalyst for the Conversion of Carbon Monoxide


by


Hiroshi Takeda

Troy Walsh

and

Jon P. Wagner

Catalyst for the Conversion of Carbon Monoxide
Inventor: Takeda et al
Atty. Docket: 20020802-004B

## CROSS-REFERENCE TO RELATED APPLICATIONS

The present application is related to U.S. Provisional Application Serial Number 60/516,230 filed on

October 31, 2003 and incorporated herein in its entirety by reference.

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## BACKGROUND OF THE INVENTION

1.    Field of the Invention

The present invention is for a catalyst for the conversion of carbon monoxide. More

specifically, this invention relates to catalyst comprising a support having a predetermined pore size and a

10    metal capable of forming a metal carbonyl species. In one embodiment, the catalyst of the present invention

comprises a mordenite, beta, or faujasite support and ruthenium metal.

2.    Description of the Related Art

In a fuel cell, such as a Polymer Electrolyte Membrane Fuel Cell (PEMFC) stack, chemical energy of a

15    fuel is converted into electrical energy. Typically, the fuel used is a hydrogen rich gas supplied to the fuel cell

by a fuel processor. However, the gas from the fuel processor may further comprise unconverted hydrocarbon,

water, carbon dioxide and carbon monoxide. The carbon monoxide, in particular, is detrimental to the PEMFC

stack because the carbon monoxide can poison the noble metal electrodes utilized by the fuel cells, thereby
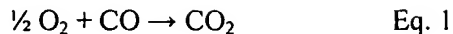
reducing the electrical output.

20    Preferably, the CO concentration for a fuel cell feed should be at a level below about 100 ppm, and

more preferably to a level of less than about 50 ppm. However, as received from the fuel processor, the CO

concentrations may be in excess of about 1 wt%, thus requiring further reduction of CO concentration. Some

typical methods for reducing the CO concentration include selective catalytic oxidation of CO, pressure swing

adsorption, hydrogen separation by membrane, and selective methanation of CO.

25    Selective catalytic oxidation of CO (Eq. 1) is a well-known process for reducing the CO concentration

for fuel cells. But, oxidation of hydrogen (Eq. 2) is a competitive reaction.

Catalyst for the Conversion of Carbon Monoxide
Inventor: Takeda et al
Atty. Docket: 20020802-004B

$$\tfrac{1}{2} O_2 + CO \rightarrow CO_2 \qquad\qquad \text{Eq. 1}$$

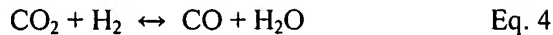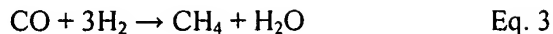$$\tfrac{1}{2} O_2 + H_2 \rightarrow H_2O \qquad\qquad \text{Eq. 2}$$

Thus, in order to maximize the concentration of hydrogen gas and minimize the concentration of carbon

monoxide, it is necessary to have reaction conditions wherein Eq. 1 is favored over Eq. 2. One option for

5     achieving this is to have a highly specific catalyst for the oxidation of carbon monoxide and to limit the oxygen

concentration so that the oxygen is consumed primarily for the production of carbon dioxide. Theoretically,

this is achievable, but in practice there are wide swings in the CO concentrations produced by the fuel

processor and it can be difficult to adjust the oxygen input to track the CO concentration. Because the CO is

more detrimental to the fuel cell than water, it is typical for excess oxygen to be fed into the reactor thereby

10    essentially ensuring that the CO will be converted to $CO_2$. The disadvantage is that significant quantities of $H_2$
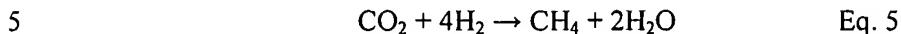
are converted to water by operating in this manner.

Pressure swing adsorption is an industrially proven technology, but it requires relatively high pressure

operation. Thus, while this process may be effective for use in larger fuel cells, it is not practical at this time

for smaller fuel cells.

15    Hydrogen separation by membrane is effective for separating hydrogen from carbon monoxide. But

the process requires a substantial pressure drop to effect the separation, and the cost and durability of the

membranes still must be proven.

Selective methanation (Eq. 3) is a process whereby carbon monoxide is reacted with hydrogen in the

presence of a catalyst to produce methane and water and methanation of carbon dioxide is minimized.

20    Commonly used in ammonia plants, total carbon oxide methanation is known to reduce carbon monoxide and

carbon dioxide concentrations to levels as low as about 5 ppmv to 10 ppmv, and the industrial catalysts are not

selective. However, in most fuel cell applications, the selective methanation reaction is accompanied by a

reverse water-gas-shift reaction (Eq. 4), which also is generally facilitated by a catalyst. Thus, while the CO

concentration is being reduced through methanation, additional carbon monoxide is formed from the carbon

25    dioxide present to maintain the equilibrium of the water-gas-shift reaction.

Catalyst for the Conversion of Carbon Monoxide
Inventor: Takeda et al
Atty. Docket: 20020802-004B

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad\qquad Eq. 3$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad\qquad Eq. 4$$

Under the proper reaction conditions and with a non-selective methanation catalyst, the $CO_2$ may be methanated as shown in Eq. 5.

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$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad\qquad Eq. 5$$

But, this is generally an undesirable reaction because it further consumes $H_2$ and the $CO_2$ methanation is normally accompanied by a temperature rise in the reactor that can lead to "run-away" conditions. Considering that the carbon dioxide concentration is greater than 10 times that of carbon monoxide, achieving selectivity is not thermodynamically favorable. Thus, it would be advantageous to have a catalyst that is highly selective for

10 CO methanation, essentially suppresses $CO_2$ methanation and does not facilitate the conversion of $CO_2$ to CO through the water-gas-shift reaction.

In the prior art methanation processes, precious metals supported on non-zeolitic materials, such as $Al_2O_3$, $SiO_2$, and $TiO_2$, have been used as catalysts in the selective methanation of CO (see, for example, U.S. Pat. No. 3,615,164 and U.S. Pat. Pub. No. 2003/0086866). For example, in Patent Number WO 01/64337,

15 ruthenium (Ru) on a carrier base support of $Al_2O_3$, $TiO_2$, $SiO_2$, $ZrO_2$, or $Al_2O_3$-$TiO_2$ with egg-shell structure is taught to reduce the CO to concentrations of about 800 ppm with 70-80% selectivity under an atmosphere of CO at 0.6%, $CO_2$ at 15%, $H_2$ at 64.4%, $H_2O$ at 20% and GHSV = 10,000 $H^{-1}$. However, for an efficient PEMFC power system, the CO concentration should be less than about 100 ppm, and preferably equal to or less than about 50 ppm. Since the CO concentration from the selective methanation processes using the prior

20 art catalysts are significantly higher than the desired maximum concentration for a PEMFC stack, these catalysts cannot be practically used in PEMFC power systems.

Thus, it would be advantageous to have a catalyst that is highly selective for CO methanation, essentially suppresses $CO_2$ methanation and does not facilitate the conversion of $CO_2$ to CO through the water-gas-shift reaction.

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Catalyst for the Conversion of Carbon Monoxide
Inventor: Takeda et al
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## SUMMARY OF THE INVENTION

The catalyst of the present invention comprises a metal capable of forming a metal-carbonyl species on a support having a predetermined pore size. More specifically, the catalyst comprises a metal selected from the group consisting of ruthenium, rhodium, nickel, iron, cobalt, rhenium, palladium, lead, tin and other metals

5    that form a metal-carbonyl species on a support having a regular lattice structure and a predetermined pore diameter of sufficient dimensions to accommodate the carbonylated metal species. In an embodiment, the metal is ruthenium and the support is selected from mordenite, beta-zeolite or faujasite and has a pore diameter of greater than about 6.3Å, and a pore volume in the range of from about $0.3 cm^3/g$ to about $1.0 cm^3/g$. An inert binder, such as alumina, $\gamma$-$Al_2O_3$, $SiO_2$, $ZrO_2$, $TiO_2$ or pseudo-boehmite, may optionally be added to the

10   catalyst. The catalyst efficiently facilitates the selective hydrogenation of carbon monoxide using $H_2$ that is present in the reformate and reduces the concentration of the CO to levels equal to or less than about 50 ppm.

The present invention further includes a process for CO "polishing", whereby the concentration of CO in a mixture of gases containing hydrogen, hydrocarbons, carbon dioxide, carbon monoxide and water is removed or substantially reduced. Particularly, this invention is directed to a method of selective methanation

15   whereby carbon monoxide is reduced to a concentration level such that the residual hydrogen is suitable for use as a fuel in a fuel cell and the overall efficiency of the PEMFC power system is improved.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The catalyst of the present invention has demonstrated benefits in facilitating the carbon oxide

20   methanation reactions in small fuel cells. In general terms, the catalyst comprises a metal capable of forming a metal-carbonyl species on a support having a predetermined pore size of sufficient dimensions to allow the pore to accommodate a fully carbonylated metal complex. As is known in the art, some typical supports for catalysts are crystalline alumino-silicate materials. Among the metals known in the art to form stable metal-carbonyl complexes are ruthenium, rhodium, nickel, iron, cobalt, rhenium, palladium, lead and tin, as an

25   exemplary group. Optionally, an inert binder, such as alumina, $\gamma$-$Al_2O_3$, $SiO_2$, $ZrO_2$, $TiO_2$ or pseudo-boehmite,

Catalyst for the Conversion of Carbon Monoxide
Inventor: Takeda et al
Atty. Docket: 20020802-004B

may optionally be added to the catalyst.

The present invention will be described herein through, without limitation, exemplary embodiments, figures and examples. Any embodiments, figures, examples and related data presented herein are merely to exemplify the principles of the invention, and are not intended to limit the scope of the invention.

5       The support of the catalyst of the present invention comprises a crystalline alumino-silicate having a predetermined pore size. More specifically, the crystalline alumino-silicate can be a molecular sieve, beta-zeolite, mordenite, faujasite or any other alumino-silicate with a regular lattice structure. Other supports that also have regular lattice structures and essentially consistent pore sizes that may be used in place of the alumino-silicate for the catalyst of the present invention include alumina, titania, ceria, zirconia and

10     combinations thereof. Because it is believed that the methanation reaction occurs within the support pore, the pore must be of sufficient dimensions to accommodate a fully carbonylated metal complex, and thus, the pore size requirement will vary depending on the metal species selected for the catalyst. However, it has generally been observed that if the pore size is smaller than or is significantly larger than the dimensions of the fully carbonylated metal species, the resulting catalyst does not show the desired selectivity for carbon monoxide

15     methanation.

The metal of the catalyst of the present invention must be capable of forming a metal-carbonyl species. As is known in the art, metals may form metal-carbonyl complexes wherein each ligand is a carbonyl unit, such as $Fe(CO)_5$, or metals may form metal-carbonyl complexes wherein at least one ligand is not a carbonyl, such as $CpFe(CO)_3$. For the purpose of the development, it is not necessary that the metal be capable of

20     forming a fully-carbonylated complexes, *e.g.* wherein each ligand is a carbonyl group. Rather, a "fully-carbonylated" complex – for the purpose of calculating the volume needed within the support pore – is defined herein as the metal complex with the maximum number of carbon monoxide ligands that the metal prefers to accommodate in its lowest energy state. The metal is preferably selected from the group consisting of ruthenium, rhodium, platinum, palladium, rhenium, nickel, iron, cobalt, lead, tin, silver, iridium, gold, copper,

25     manganese, zinc, zirconium, molybdenum, other metals that form a metal-carbonyl species and combinations

Catalyst for the Conversion of Carbon Monoxide
Inventor: Takeda et al
Atty. Docket: 20020802-004B

thereof. As delivered to the catalyst, the metal may be a base metal or it may be a metal oxide complex.

The metal may be added to the support by any means known in the art for intercalating the metal into the support pores, such as, without limitation, impregnation, incipient wetness method, immersion and spraying. The embodiments presented herein add the metal through impregnation for exemplary purposes

5      only. Although not a requirement to practice the invention, it is recommended that the metal source be free of typically recognized poisons, such as sulfur, chlorine, sodium, bromine, iodine or combinations thereof. Acceptable catalyst can be prepared using metal sources that include such poisons, but care must be taken to wash the poisons from the catalyst during production of the catalyst.

In an embodiment of the present invention, the support is a crystalline alumino-silicate selected from

10     mordenite, beta-zeolite or faujasite. The support has a pore diameter of greater than about 6.3Å, and a pore volume in the range of from about $0.3 cm^3/g$ to about $1.0 cm^3/g$, and preferably in the range of $0.5 cm^3/g$ to about $0.8 cm^3/g$. Ruthenium is impregnated on the support so as to deliver a concentration of from about 0.5 wt% Ru to about 4.5 wt% Ru, based on the total weight of the catalyst including the ruthenium. Some recommended sources of ruthenium include, without limitation, $Ru(NO)(NO_3)_x(OH)_y$, $Ru(NO_2)_2(NO_3)_2$, $Ru(NO_3)_3$, $RuCl_3$,

15     $Ru(CH_3COO_3)$, $(NH_4)_2RuCl_6$, $[Ru(NH_3)_6]Cl_3$, $Ru(NO)Cl_3$, and $Ru_3(CO)_{12}$. Optionally, the catalyst further comprises the binder $\gamma-Al_2O_3$ at a loading of about 20 wt%, including the weight of the binder. The catalyst may be used in an exemplary process for removing or substantially reducing the quantity of carbon monoxide in a mixture of gases containing hydrogen, carbon dioxide, carbon monoxide, and water. The process involves passing a mixture of gases over the catalyst in a reaction zone having a temperature below the temperature at

20     which the shift reaction occurs and above the temperature at which the selective methanation of carbon monoxide occurs.

It is understood that variations may be made which would fall within the scope of this development. For example, although the catalysts of the present invention are intended for use as selective methanation catalysts for the conversion of carbon monoxide for fuel cell applications, it is anticipated that these catalysts

25     could be used in other applications requiring highly selective carbon oxide methanation catalysts.